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RESEARCH MEMORANDUM

CORRELATION BETWEEN HYDROGEN PRESSURE AND PROTECTIVE
ACTION OF ADDITIVES IN THE MOLTEN SODIUM
HYDROXIDE - NICKEL SYSTEM

By Charles E. May

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ACTION OF ADDITIVES IN THE MOLTEN SODIUM

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SUMMARY

The effect of various metallic additives (chromium, aluminum, molybdenum, manganese, and titanium) upon the molten sodium hydroxide - nickel system was investigated. The hydrogen evolved from such systems was measured; this evolution was correlated with the effect of the metal on mass transfer. It was concluded that the beneficial properties of chromium were not due to the chromium metal itself nor to the hydrogen directly produced from it. The data indicated that the inhibition of mass transfer is due to the presence and/or the reaction of the chromite radical (CrO_3^{-3}) or similar species that was produced from the metallic chromium.

INTRODUCTION

The sodium hydroxide - nickel system is being investigated because it is a possible heat-transfer system at high temperatures. Under such temperatures, mass transfer of nickel occurs from regions of higher temperature to regions of lower temperature. The addition of certain metallic powders (chromium (refs. 1 and 2) and aluminum (ref. 1)) decreases the rate of the phenomenon.

This investigation is intended to correlate the beneficial qualities of these additives with the hydrogen produced during the tests under question, since hydrogen itself is known to be beneficial (ref. 3).

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Since it was thought at one time that other-metallic powders might have the same beneficial effects as Cr and Al, manganese, molybdenum, and titanium were also investigated. The system used was designed to measure the hydrogen evolved in the standard nickel crucible test used at the NACA Lewis laboratory (refs. 1, 4, and 5) without disturbing conditions more than necessary, lest reproducibility be lost. Conditions for all tests were kept as nearly alike as the experimentation would permit.

The runs were 80 hours long; the additives were used in various concentrations, 1/2 to 5 percent; tests with no additives were also run. The hydrogen evolved was measured by reading the pressure developed in Inconel chambers in which the standard nickel crucibles were encased. The amount of hydrogen evolved was likewise measured by the losses in weight of the nickel crucibles that occurred during the run. To correlate these tests with the previous standard ones, nickel specimens were included in the nickel crucibles.

APPARATUS AND PROCEDURE

The apparatus, a schematic diagram of which is given in figure 1, consisted of a special Globar furnace containing four Inconel chambers. Inside each chamber was a sealed nickel crucible containing the sodium hydroxide and additive. During the runs, the hydrogen gas generated by the reaction of the additive with sodium hydroxide diffused through the crucible walls and was measured by means of the pressure exerted within its respective Inconel chamber.

Nickel Crucibles

The inner crucibles were fabricated from "L" nickel tubing. These crucibles were identical in construction to those described in previous reports (refs. 1, 4, and 5). They were 5 inches long, with a 5/8-inch outside diameter and a 1/16-inch wall thickness. A 5/16-inch-diameter specimen and all the crucible components (except vent tubes) were made from the same length of tubing. Before welding, the components were cleaned in a modified aqua regia solution for 2 minutes. Heliarc welding with helium plus 15 percent hydrogen atmosphere was used in fabrication. A flow of argon was maintained in the tube during welding in order to prevent oxidation.

Sodium hydroxide was weighed (13.0 ± 0.1 g) into the crucible in a dry box. The top and vent tubes were then welded into place. The moisture and air were removed by evacuation first at about 540° F (to 5 microns) and then at about 720° F (to 5 microns). When evacuation was completed, a cover gas of helium at 2 pounds per square inch gage was admitted.

On some runs the additive (as 325-mesh powder) was placed in the crucible when the sodium hydroxide was added; for others, the additive was added in a dry box after the above-mentioned evacuation (purging) treatment. The dry-box atmosphere was then removed by evacuation and a fresh supply of cover gas admitted. The vent tube (on the top) was crimped, and welding of the crimp sealed the crucible. A Nichrome loop was then spot-welded to the stem so it could be easily placed within the Inconel chamber.

Inconel Chambers

The Inconel chambers were made of tubing $19\frac{1}{2}$ inches long with an inside diameter to allow for about 0.007-inch tolerances for the 5/8-inch nickel crucibles inside. The wall thickness was a little under 1/16 inch. The bottoms were 1/16-inch Inconel welded to the tubing. The tops were made of brass, with soft-soldered sealing to enable easy removal of the inner nickel crucibles. The tops of the chambers were outside of the furnace and cool enough that the soft solder did not melt. Connection to a glass vacuum system was made through 1/4-inch copper tubing and through waxed standard tapered joints (brass to glass). Thermocouples were attached to the Inconel chambers at the sodium hydroxide liquid level and at a point about 1/8 inch from the bottom. Each of the four Inconel chamber systems (used for each run) could be isolated from the central vacuum system through glass stop-cocks. Included in each system were Bourdon-type and thermocouple vacuum gages. These were calibrated against a mercury manometer and a McLeod gage connected to the central vacuum system. Evacuation of the entire system was accomplished by a forepump, a three-stage mercury diffusion pump, and a liquid-nitrogen cold trap.

Furnace

The specially designed furnace used is described in reference 1. Since the chambers were permanently and rigidly connected to the vacuum system, the furnace itself had to be moved upward into place. This was done by means of an air-powered hoist.

Test Procedure

The four Inconel chambers were mounted symmetrically above the furnace, with each crucible $3\frac{5}{8}$ inches from its nearest neighbor. One weighed nickel crucible was inserted into each chamber by means of a

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hooked probe; the brass caps were soldered on; the system was checked for leaks and then evacuated to about 5 microns with the crucibles at about 600° F. The stopcocks between each crucible system and the central vacuum system were closed; the furnace, which was already at the test temperature, was raised into position. The temperature at the bottom of the Inconel chambers reached 1400° F generally in about 20 minutes. Since at this time the pressure developed in the Inconel chambers became measurable on the Bourdon-type gages, the timing of the run was begun at this point. About 10 minutes more was required for the temperature at the bottom of the chambers to reach 1500° F, at which temperature they were controlled.

At the end of 80 hours, the furnace was lowered and the crucibles were quenched in water. During the run, pressures were read on the calibrated Bourdon-type gages. If the pressure became too low near the end of a run to be read accurately on these, the gas in any one of the chamber systems was expanded into a part of the central vacuum system of known volume by opening the stopcock for 10 seconds and then closing. The pressure in the central system was then read on a McLeod gage. The pressure originally in the chamber was calculated from this value. In order to calculate the loss in weight due to hydrogen escape (table I), the nickel crucible was weighed before and after the run. The contents were washed out with boiled distilled water. Some of these water solutions were chemically analyzed. The specimen in the crucible was also weighed before and after the run.

Calibration of Volumes and Rate of Diffusion

The volumes of the Inconel chamber systems were calibrated with helium gas while the crucibles were at the test temperature. The effective volumes are listed in column 3 of table II.

Since the hydrogen formed during a run diffuses through the Inconel of the chamber, the rate of this diffusion r_1 (mg/hr) was experimentally determined by admitting a known amount of hydrogen into each chamber and measuring the change of pressure as a function of time. The resultant relation between r_1 and P (pressure within Inconel chambers) given in figure 2 can be expressed in the form

$$r_1 = aP^b$$

RESULTS AND DISCUSSION

Check with Standard Tests

3885 The results of specimen weight changes show that conditions differed slightly from the standard static corrosion test used at the Lewis laboratory. The weight loss of a specimen in the present tests without additives is 4.7 ± 0.7 mg/80 hours (see table I) or 1.4 ± 0.2 mg/24 hours as compared with 5.9 ± 0.6 mg/24 hours for the standard test. The observed temperature difference along the outer Inconel tube was about 80° F compared with 45° F for the standard test (i.e., with no Inconel tube surrounding the nickel and with thermocouples welded directly to the nickel). The weight losses of specimens in crucibles with additives indicate that in the present tests only chromium was an effective inhibitor of mass transfer.

Purging

Chromium, aluminum, manganese, and molybdenum did not appreciably react with sodium hydroxide at 720° F (i.e., during purging). On the contrary, titanium evolved hydrogen during this procedure.

Presence of Two Valences for Chromium

A straight line with a slope of unity should result if the loss in weight of the crucible is plotted against the weight of hydrogen generated by the reaction of the additive with the caustic as calculated from the amount of additive used (column 7, table I), assuming the proper valences (see fig. 3). The proper valences were found to be as follows: Cr, 3.5; Mo, 6; Al, 3; Ti, 3; Mn, 2. The apparent nonintegral valence for chromium indicates the presence of at least two different valences for chromium. The most logical ones are +3 and +6. This is supported by the analysis of the reaction products; the water solution from four crucibles (1 to 3 percent Cr) showed 18.5 ± 1.7 percent chromate (Cr^{+6}) to be present; the rest appears to be chromite (Cr^{+3}). This would lead to an effective average valence change of 3.55 ± 0.05 .

The fact that the curve in figure 3 does not pass through the origin is most probably due to loss of air and moisture adsorbed originally on the nickel crucibles.

Reaction Time of Additive

The hydrogen pressures developed within typical crucible systems are shown graphically as a function of time in figure 4. Pressures developed in runs without additives were so small that no correction for them was made on the additive runs.

The rate r_2 (mg/hr) at which hydrogen escapes from the nickel crucibles is equal to the rate of build-up in the Inconel chambers plus the rate of diffusion out of the Inconel r_1 . The r_2 thus calculated were plotted as a function of time as shown in figure 5. In the dashed-line regions the rate of hydrogen diffusion through the walls of the nickel crucibles was retarded because of the hydrogen accumulated in the Inconel chambers. For this reason the values of r_2 were uncertain in these regions. Such uncertainties were not significant to this research.

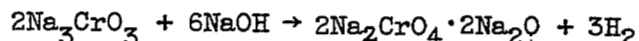
The rate of production of hydrogen from the chemical reaction between sodium hydroxide and the additive used is equal to this rate of transfer of hydrogen out of the nickel crucibles when it is a maximum; the temperature is assumed to be constant. The maximum rate occurred near the beginning of the experiment (fig. 5); these values are listed in column 4 of table II. On the assumption that the rate of reaction of the metal with sodium hydroxide is very roughly constant with time (as a consequence of being a heterogeneous reaction), the maximum lives of the additives as the free metals were those listed in column 7 of table II. These lifetimes (1/2 to 4 hr) are short compared with the time for which chromium is effective as an inhibitor (250 hr, ref. 2). It is concluded, therefore, that metallic chromium itself is not the inhibiting factor in mass transfer. In addition, the hydrogen produced directly by the reaction of chromium with caustic cannot be the beneficial agent, since crucibles containing other additives that produce hydrogen in a similar manner do not show the beneficial features.

The values in table II likewise indicate the relative reactivity of the four metals investigated; the reactivity increases in this order: Cr < Mo < Al < Ti.

Pressure within Nickel Crucibles

Relative pressures within nickel crucibles can be calculated from the values of r_2 if the common rate law of diffusion ($r_2 = e\sqrt{P}$, ref. 6) be used. The relative pressures at 80 hours for additions of Cr, Mo, Al, and Ti were thereby calculated using the lowest pressure value found as unity (table III).

The existence of hydrogen pressures at 80 hours which are an order of magnitude greater for additions of 3 to 5 percent chromium than for any other additives is of interest. This is taken as evidence that a hydrogen-producing reaction is occurring even after long periods of time. Since the chromium metal had long since reacted, this reaction must be one involving a product from the initial reaction of chromium with the caustic. The fact that chromite and chromate were found in the melts leads to the conclusion that the following reaction is occurring:



It may thus be possible that the inhibiting action of chromium is due to the hydrogen generated by the reaction of the chromite, which has a relatively long lifetime in sodium hydroxide.

SUMMARY OF RESULTS

The effect of various metallic additives (Cr, Mo, Al, Ti, and Mn) upon the molten sodium hydroxide - nickel system was studied. The hydrogen evolved was measured and correlated with the effect of the metal on mass transfer. The conclusion drawn was that the beneficial properties of chromium were not due to the chromium metal itself, since it was used up in less than 4 hours. In addition, the hydrogen produced directly by the reaction of chromium with caustic could not be the beneficial agent, since crucibles containing the other additives show production of hydrogen in a similar manner but do not show any inhibition of mass transfer.

Instead, the data indicated that the inhibition was due to the reaction of chromite (CrO_3^{-3}) or similar species present in the sodium hydroxide. The basis for this was the fact that both chromite and chromate were found in the crucibles after a run as well as the fact that hydrogen was still being produced after long periods of time in crucibles with chromium additions.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 8, 1955

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2. Forestieri, Americo F., and Lad, Robert A.: The Use of Metallic Inhibitors for Eliminating Mass Transfer and Corrosion in Nickel and Nickel Alloys by Molten Sodium Hydroxide. NACA RM E54L13, 1955.
3. Lad, Robert A., and Simon, Sidney L.: A Study of Corrosion and Mass Transfer of Nickel by Molten Sodium Hydroxide. Corrosion, vol. 10, no. 12, Dec. 1954, pp. 435-439.
4. Mosher, Don R., and Lad, Robert A.: Kinetic Study of Mass Transfer by Sodium Hydroxide in Nickel under Free-Convection Conditions. NACA RM E53K24, 1954.
5. Forestieri, Americo F., and Zelezny, William F.: Static Crucible Investigation of Corrosion and Mass-Transfer of Nickel in Molten Sodium Hydroxide with Various Additives. NACA RM E53F12, 1953.
6. Barrer, Richard M.: Diffusion in and through Solids. Cambridge Univ. Press (London), 1941, pp. 169-178.

TABLE I. - CRUCIBLE DATA

Crucible	Additive	Weight of additive, g	Additive, approx. percent	Specimen weight change, g	Crucible weight change, g	Weight of hydrogen evolved based on amount of additive, g
9	-----	-----	1	-0.0055	-0.0040	-----
10	^a Cr	0.1284	1	-.0086	-.0127	0.0087
11	^{a,b} Cr	.2598	2	+.0008	-.0234	.0176
12	^a Cr	.3903	3	+.0012	-.0284	.0265
53	^a Cr	.1296	1	-.0048	-.0134	.0088
54	^a Cr	.3898	3	+.0027	-.0315	.0264
55	^a Cr	.6504	5	+.0004	-.0476	.0441
56	^{a,b} Cr	1.1714	9	-.0135	-----	-----
37	Mo	.1307	1	-.0585	-.0102	.0082
38	Mo	.2647	2	-.1058	-.0195	.0167
39	^a Mo	.1326	1	-.0267	-.0085	.0084
40	^a Mo	.2598	2	-.0930	-.0178	.0164
13	-----	-----	1	-.0036	-.0046	-----
14	^a Al	.0651	$\frac{1}{2}$	-.0077	-.0103	.0073
15	^a Al	.1277	1	-.0037	-.0163	.0143
16	^a Al	.1904	$\frac{1}{2}$	-.0041	-.0201	.0214
45	Ti	.1305	1	-.0073	-.0120	.0082
46	Ti	.1953	$\frac{1}{2}$	-.0103	-.0174	.0123
47	Ti	.1313	1	-.0082	-.0122	.0083
48	Ti	.1969	$\frac{1}{2}$	-.0133	-.0168	.0124
17	-----	-----	1	-.0050	-.0018	-----
18	^{a,c} Ti	.0651	$\frac{1}{2}$	-.0092	-.0001	-----
19	^{a,c} Ti	.1302	1	-.0098	-.0018	-----
20	^{a,c} Ti	.1951	$\frac{1}{2}$	-.0118	-.0028	-----
33	Mn	.1334	1	-.0173	-.0082	.0049
34	Mn	.2673	2	-.0481	-.0139	.0098
35	^a Mn	.1301	1	-.0224	-.0080	.0048
36	^a Mn	.2602	2	-.0235	-.0127	.0095

^aPurged with additive.^bLeak.^cHydrogen evolved on purging.

TABLE II. - LIFETIMES OF ADDITIVES

Crucible	Additive	Volume of system, cc	Maximum rate of hydrogen evolution, mg/hr	Total amount of hydrogen evolved, mg	Rate of generation of hydrogen, percent/hr	Life of additive, hr
10	Cr	130	2.2	8.7	25	4.0
12	Cr	130	10	26.5	38	2.6
53	Cr	160	5.0	8.8	57	1.8
54	Cr	160	14	26.4	53	1.9
55	Cr	160	35	44.1	79	1.3
37	Mo	160	9.9	8.2	121	.83
38	Mo	160	17	16.7	102	.98
39	Mo	160	9.9	8.4	118	.85
40	Mo	160	17	16.4	104	.96
14	Al	130	11	7.3	150	.67
15	Al	130	16	14.3	112	.89
16	Al	130	26	21.4	122	.82
45	Ti	160	15	8.2	183	.55
46	Ti	160	21	12.3	171	.58
47	Ti	160	15	8.3	181	.55
48	Ti	160	19	12.4	153	.65

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TABLE III. - PRESSURE WITHIN NICKEL CRUCIBLES

Crucible	Additive	Percent of additive	H ₂ escape rate, r ₂ , mg/hr at 80 hr	Relative pressures at 80 hr
10	Cr	1	0.013	1.4
12	Cr	3	.063	33
53	Cr	1	.029	7.0
54	Cr	3	.040	13
55	Cr	5	.060	30
38 to 40	Mo	1 and 2	.021	3.6
14	Al	$\frac{1}{2}$.011	1.0
15	Al	1	.014	1.6
16	Al	$1\frac{1}{2}$.017	2.4
45 and 47	Ti	1	.014	1.6
46 and 48	Ti	$1\frac{1}{2}$.016	2.1

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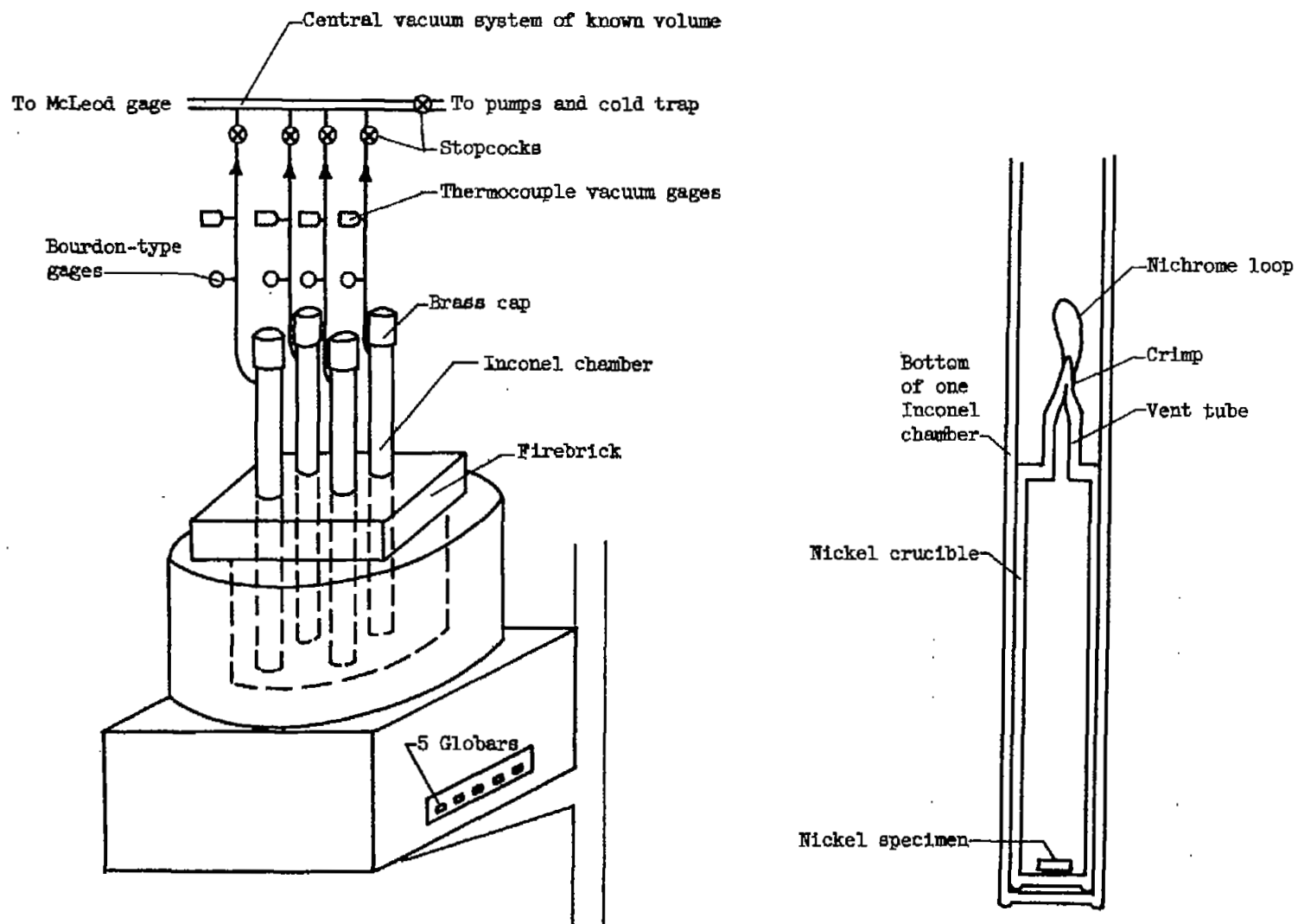


Figure 1. - Schematic diagram of apparatus (not to scale).

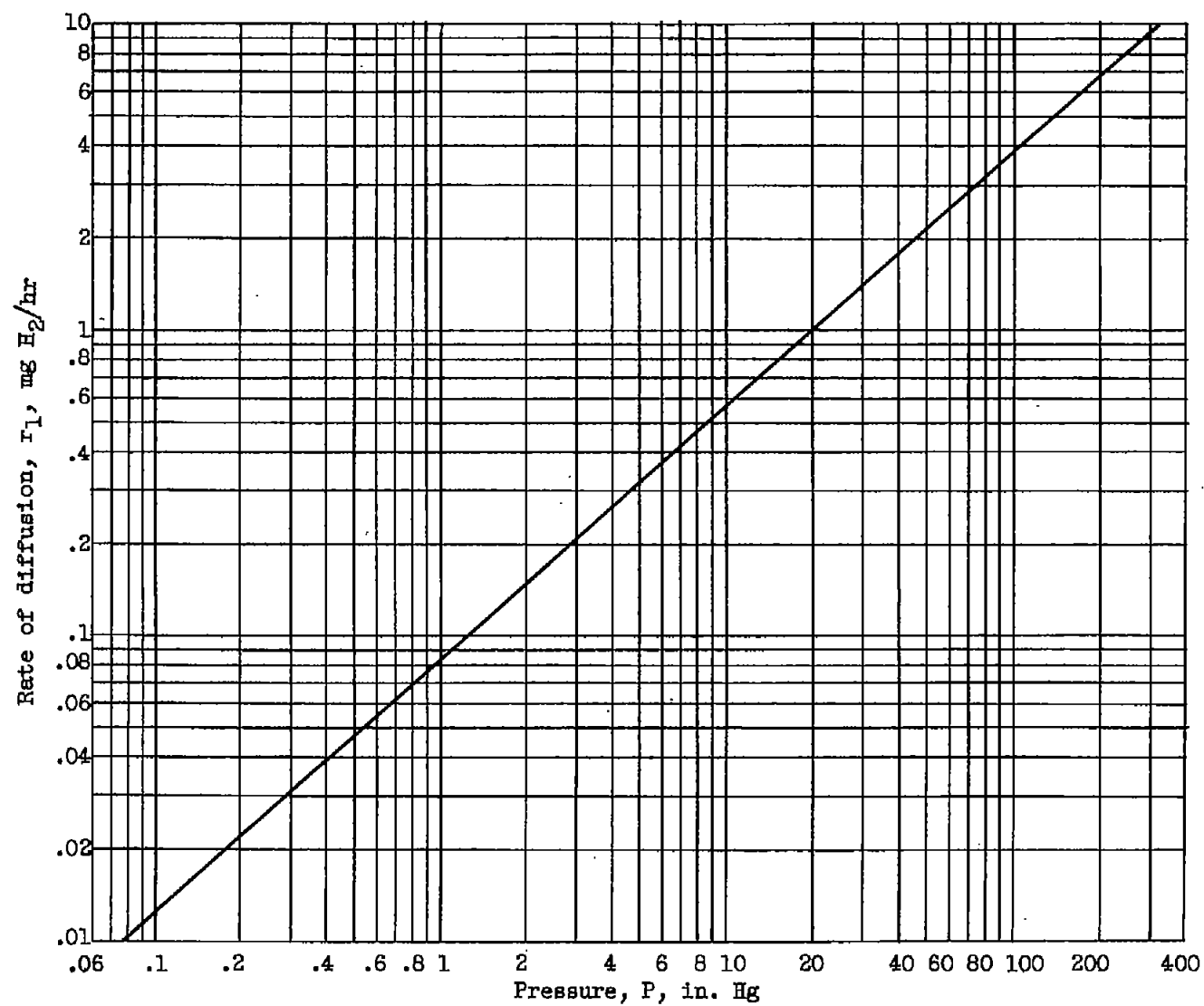


Figure 2. - Rate of hydrogen diffusion through Inconel as function of pressure.

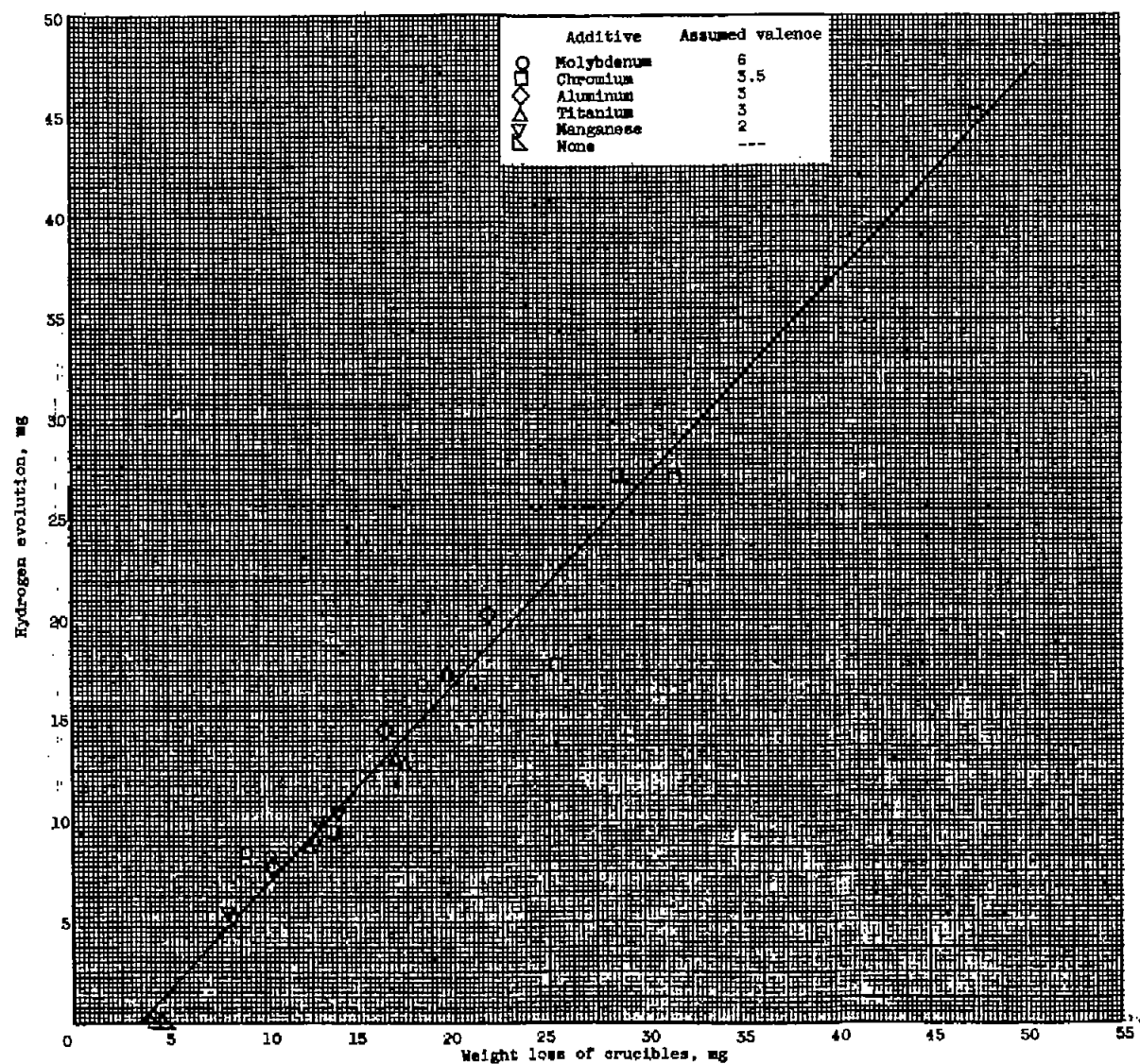


Figure 5. - Computed hydrogen loss compared with measured value.

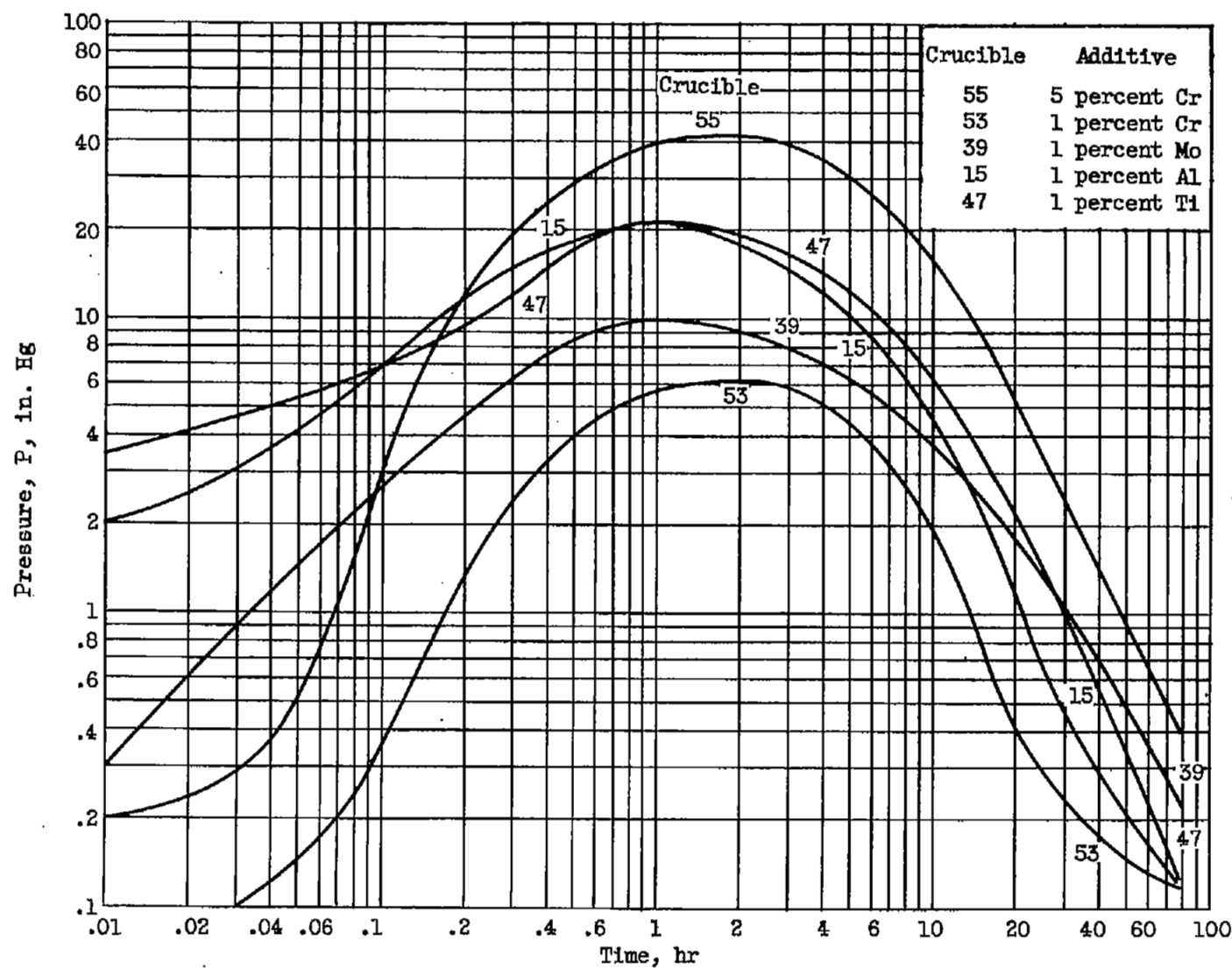


Figure 4. - Variation of pressure within Inconel crucibles with time.

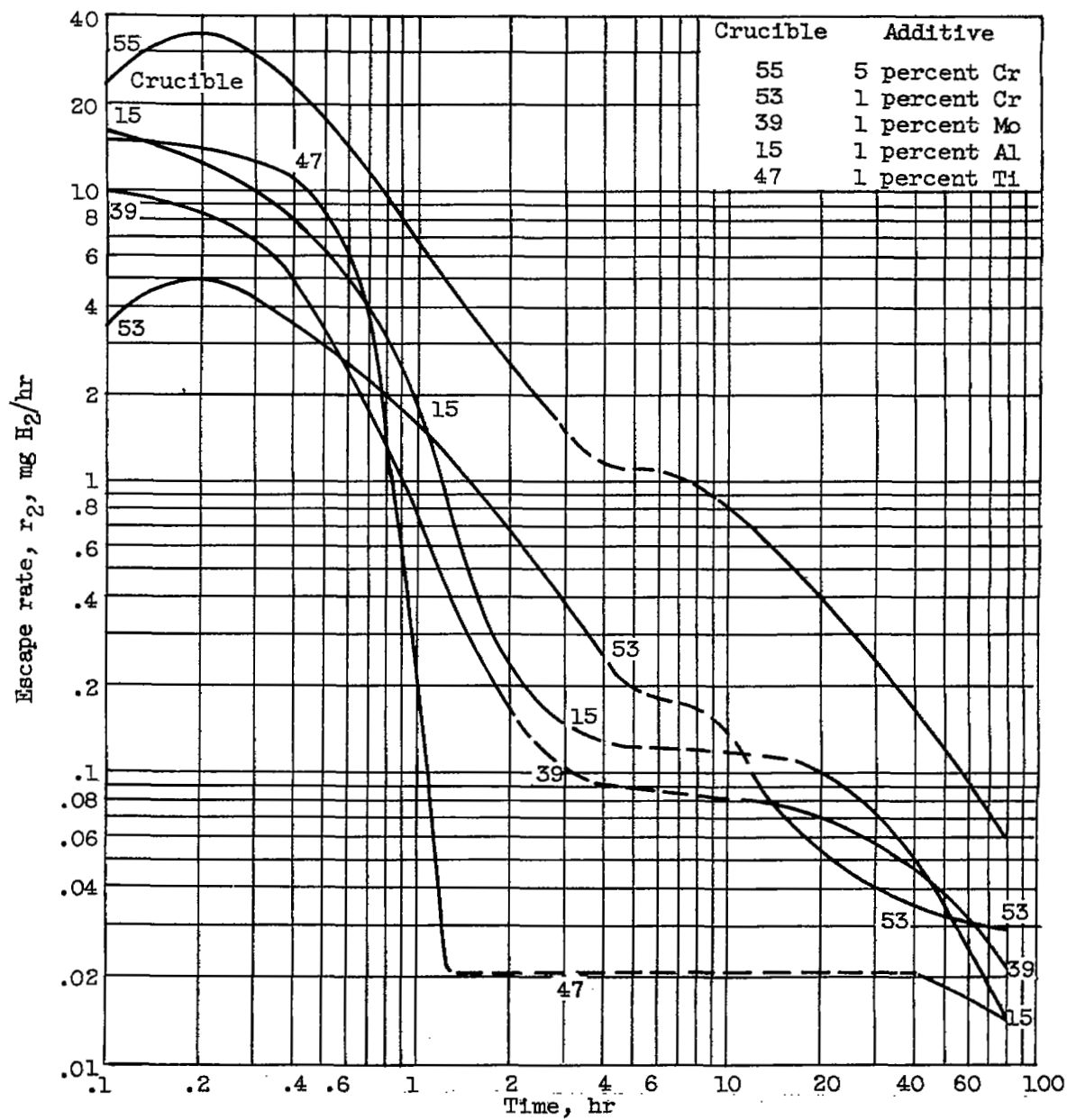


Figure 5. - Rate of hydrogen escape from nickel crucibles.

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